

Physical Chemistry Laboratory, I
CHEM 445
Experiment 5
Heat Capacity Ratio for Gases
 (Revised, 1/10/03)

The heat capacity for a substance is the amount of heat needed to raise the temperature of the substance by 1 °C or 1 K. The heat capacities depend on the chemical nature of the substance, on the physical state of the substance, on the temperature, and on whether P or V is held constant during the process: C_P or C_V .

For liquids and solids, $C_V \approx C_P$ and the two terms are often used interchangeably. However, for ideal gases, it is well known (Tinoco, Jr., Sauer, and Wang or Noggle) that

$$\bar{C}_P = \bar{C}_V + R \quad (1)$$

In this equation, \bar{C} = molar heat capacity of the gas, either at constant pressure or at constant volume. The bar over a symbol refers to that quantity per mol of substance. The molar heat capacities are defined by the equations,

$$\bar{C}_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V \quad \text{and} \quad \bar{C}_P = \left(\frac{\partial \bar{H}}{\partial T} \right)_P \quad (2)$$

For a monatomic gas, there is no rotational or vibrational energy and if the temperature is relatively low, only the ground electronic state of the species is populated to any extent. Consequently, only translational energy is involved; and from kinetic theory,

$$\bar{C}_V = \frac{3R}{2} \quad \text{and} \quad \bar{C}_P = \frac{5R}{2} \quad (3)$$

For polyatomic gases, there are additional forms of energy that contribute to the heat capacity.

$$\bar{E} = \bar{E}(\text{trans}) + \bar{E}(\text{rot}) + \bar{E}(\text{vib}) \quad (4)$$

For many simple diatomic molecules, however, the vibrational contribution to the heat capacity is small, and in the neighborhood of room temperature, $C_V = \frac{5R}{2}$. However, the heat capacities of diatomic molecules increase with increasing temperature as the vibrational modes become active.

The heat capacities of polyatomic molecules are more complex and less predictable. The equipartition principle predicts that the heat capacity depends on the number of vibrational degrees of freedom in the molecule that is determined by the number of atoms in the molecule. The equipartition model is incorrect in its predictions but is useful because it does indicate that the heat capacity will increase with increasing molecular complexity (number of atoms or number of bonds).

$$\bar{C}_V (\text{linear, } N \text{ atoms}) = 5R/2 + (3N - 5)R \quad (5)$$

$$\bar{C}_V (\text{non-linear, } N \text{ atoms}) = 3R + (3N - 6)R \quad (6)$$

Heat capacities play a prominent part in the Carnot cycle for determining the efficiency of an engine. For the reversible adiabatic expansion of one mol of a perfect gas,

$$d\bar{E} = -P d\bar{V} \quad \text{and} \quad d\bar{E} = \bar{C}_V dT \quad \text{and} \quad P = \frac{RT}{\bar{V}} \quad (7)$$

These equations can be combined and integrated to give the standard equation found in most physical chemistry texts,

$$\bar{C}_V \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right) \quad (8)$$

There is a predicted and observed decrease in temperature for the reversible adiabatic expansion of an ideal (or any) gas.

There is a classical experiment for the determination of the ratios of the heat capacities of gases, $C_p/C_V = \gamma$, based on rapidly releasing a gas from a large container at a pressure somewhat higher than atmospheric pressure, P_1 , until the gas reaches atmospheric pressure, P_2 . The temperature of the gas decreases during this adiabatic expansion. The container is quickly closed and the gas returns to ambient temperature and the final pressure is measured, P_3 . [1, 2, 3]

There are two theoretical developments for the analysis of this experiment. In one case the experiment is treated as a reversible adiabatic expansion of a gas (considered in this case to be ideal) from P_1 and T_1 to P_2 and T_2 followed by warming the gas at constant volume to the initial temperature, T_1 and final pressure, P_3 .

If one substitutes $R = C_p - C_V$ from Eq. (1) into Eq. (8), one obtains the following equation, in which $\gamma = \frac{\bar{C}_p}{\bar{C}_V}$.

$$\bar{C}_V \ln\left(\frac{T_2}{T_1}\right) = -(C_p - C_V) \ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right) \quad \text{or} \quad \ln\left(\frac{T_2}{T_1}\right) = -(\gamma - 1) \ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right) \quad (9)$$

Continuing with the standard development, one obtains the following equation for T and V from the adiabatic expansion of an ideal gas. Using the perfect gas equation, one can also obtain an equation relating P and V for the adiabatic expansion of an ideal gas.

$$\frac{T_2}{T_1} = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{(\gamma-1)} \quad \text{and} \quad P_1 \bar{V}_1^\gamma = P_2 \bar{V}_2^\gamma \quad \text{or} \quad \left(\frac{P_1}{P_2}\right) = \left(\frac{\bar{V}_2}{\bar{V}_1}\right)^\gamma \quad (10)$$

The gas then warms to T_1 (the initial and room temperature) at constant volume, \bar{V}_2 and P_3 . Therefore, the following equation holds.

$$P_3 \bar{V}_2 = P_1 \bar{V}_1 \quad \text{or} \quad \left(\frac{\bar{V}_2}{\bar{V}_1} \right) = \left(\frac{P_1}{P_3} \right) \quad (11)$$

Because the pressures can be measured directly, one replaces the ratio of the volumes per mol in Eq. (10) by its equivalent in terms of pressures from Eq. (11) to get the following:

$$\left(\frac{P_1}{P_2} \right) = \left(\frac{P_1}{P_3} \right)^\gamma \quad \text{or} \quad \ln \left(\frac{P_1}{P_2} \right) = \gamma \ln \left(\frac{P_1}{P_3} \right) \quad (12)$$

Eq. (12) can then be rearranged to give the final equation needed to calculate γ , the ratio of heat capacities of the gas from experimental data.

$$\gamma = \frac{\ln \left(\frac{P_1}{P_2} \right)}{\ln \left(\frac{P_1}{P_3} \right)} \quad (13)$$

In the alternative analysis [2], the process is considered as an adiabatic expansion from (P_1, T_1) against a constant pressure, P_2 , to (P_2, T_2) , and, therefore, not reversible. Then the system warms to the original temperature and a new pressure at constant volume (P_3, T_1) . For the adiabatic expansion against a constant pressure, one begins with the following differential equation (again using molar quantities for volume and heat capacity).

$$\bar{C}_v dT = -P_2 d\bar{V} \quad \text{or} \quad \bar{C}_v (T_2 - T_1) = -P_2 (\bar{V}_2 - \bar{V}_1) \quad (14)$$

One may use the perfect gas equation to replace \bar{V} and then replace R with its equivalent from Eq. 1 to obtain the following expression.

$$\bar{C}_v \left(\frac{P_2 - P_1}{P_1} \right) = -\bar{C}_p \left(\frac{P_2}{P_1} - \frac{T_2}{T_1} \right) \quad (15)$$

The temperature, T_2 , after the adiabatic expansion from P_1 to P_2 can be calculated from the perfect gas equation from the final pressure, P_3 , after the gas has returned to the initial temperature, T_1 .

$$\frac{T_2}{P_2} = \frac{T_1}{P_3} \quad (16)$$

Substituting and rearranging, one gets the following equation to calculate the ratio of heat capacities of the gas.

$$\gamma = \frac{\left(\frac{P_1}{P_2} \right) - 1}{\left(\frac{P_1}{P_3} \right) - 1} \quad (17)$$

These two equations, (13) and (17), look very different; however, they give similar results because the ratios, P_1/P_2 and P_1/P_3 are only slightly larger than one. One

can show the similarity of Eq. (13) and Eq. (17) by a Taylor's series expansion of Eq. (13) about 1.

Experimental Procedure:

The WEB is occasionally useful. You may find pictures of apparatus similar to ours on the WEB page for the University of Florida Physical Chemistry Lab, Fall, 2000. (There are probably others). Note that they do 11 experiments in their (16 week) semester: http://www.chem.ufl.edu/~itl/4411L_f00/welcome.html

You are to measure the ratio of heat capacities, γ , for two gases: N_2 and CO_2 .

The gas cylinders are in the corner of the lab and are connected to the two carboys (ballast jars) by plastic tubing. Only N_2 is used with one carboy and only CO_2 , with the other. The lines from the gas cylinders to the ballast jars should be properly connected and should not be rearranged. Check with the Lab Instructor before using the gas cylinders.

There are three valves on each rubber stopper that closes each carboy. One valve controls the line between the gas cylinder and the carboy. Another valve controls the exit from the carboy to the atmosphere. The third valve controls the connection between the carboy and the manometer. The stopper occasionally slips and should be strapped down during waiting periods. The valves on the stopper and on the gas cylinder should be tightened only "**finger-tip tight**". Do not tighten excessively: such effort does not prevent leaks and ruins the valves.

Open the gas cylinders and all valves (cylinder and top of carboy) and let the gas flow through the lines and the carboy for ~ 10 minute at a modest gas flow rate. The time and flow rate are not critical. A pressure of ~ 5 PSI (pounds per square inch) on the regulator should be sufficient.

A flow of 5 – 10 SCF/H (standard cubic feet per hour), as indicated by the flow meter, is adequate. There is a flow meter attached to each line: one on the wall by the gas cylinder and the other on the manometer at the station. Sometimes the ball sticks in the top of the flow meter and can be dislodged by a gentle tap with the base of a screwdriver. It is often useful for one person to adjust the valves on the gas cylinder and the other person to read the flow meters. If there is no gas flow, it is likely that one of the valves is closed.

After the gas has flushed the carboy for several (5 or so) minutes, reduce the flow of the gas from the cylinder coming into the carboy, slowly close the valve that lets the gas out of the carboy, and allow the pressure to increase until there is a difference of 50 – 60 cm of manometer fluid (di-n-butyl phthalate) between the two sides of the manometer. Close the valve letting gas into the cylinder (as well as the valve letting the gas out of the carboy) and turn off the fine control valve at the cylinder. If all of the valves are shut, the pressure should remain constant. Let the system sit for ~ 10 minutes for the gas to reach

room temperature (measured on a thermometer on the manometer stand), as indicated by a constant manometer reading. Record this final pressure difference, ΔP_1 , and room temperature. Record and remember this time to equilibrate for subsequent experiments.

The total pressure of the gas in the carboy, P_1 , is atmospheric pressure, P_2 , (from the barometer in the adjacent room) plus the difference in heights of the two columns on the manometer, ΔP_1 , (which must be converted from mm di-n-butyl phthalate to mm Hg). The density of di-n-butyl phthalate is 1.046 g/cm^3 at $20.0 \text{ }^\circ\text{C}$ and 1.042 g/cm^3 at $25.0 \text{ }^\circ\text{C}$. $d(\text{Hg}) = 13.596 \text{ g/cm}^3 @ 0.0 \text{ }^\circ\text{C}$, $13.546 \text{ g/cm}^3 @ 20.0 \text{ }^\circ\text{C}$, and 13.534 g/cm^3 at $25.0 \text{ }^\circ\text{C}$. Interpolate or extrapolate to obtain densities at other temperatures.

After the gas has reached room temperature (constant pressure or constant heights of the two manometer levels), remove the stopper completely from the carboy to allow the gas to expand and cool by the adiabatic expansion. Firmly replace the stopper as quickly as possible and strap down. The pressure of the gas in the carboy will then slowly increase as the gas temperature increases to the initial room temperature. It may take ~ 15 minutes for the pressure to reach a constant value. Note the time required for temperature equilibration and wait that length of time for subsequent experiments. Record this final pressure difference, ΔP_3 . The final pressure, P_3 , is atmospheric pressure, P_2 , plus ΔP_3 , converted from mm(di-n-butyl phthalate) to mm(Hg).

Repeat the set of measurements three additional times. If your four values show a trend with increasing time, the carboy was probably not flushed completely and the composition of the gas changed from one experiment to the next. Additional experiment(s) is (are) be needed. It is not necessary to duplicate pressure readings from one experiment to the next and perhaps worthwhile to use different initial pressures of the gas for the replicate experiments.

Repeat the entire process using the other gas in the other carboy.

Analysis of Data:

Prepare a table of data: ΔP_1 (mm di-n-butyl phthalate), P_1 (mm Hg), P_2 (mm Hg), ΔP_3 (mm di-n-butyl phthalate), P_3 (mm Hg), and T for each experiment with each gas. Room temperature may change somewhat during the lab period, but unless there are significant changes during the course of an experiment, no errors will be introduced. Atmospheric pressure may also change throughout the lab period and should be recorded for each experiment.

Your final results should be presented in a table that includes, P_1 , P_2 , P_3 and γ calculated from Eq. (13) and from Eq. (17). Because you have several (nominally 4) determinations for γ for each gas, calculate the average, standard deviation, and relative standard deviation for γ for each gas.

Compare your results with literature values of γ for N_2 and for CO_2 , with references for your values.

Show that Eq. (13) reduces to Eq. (17) by making a power series expansion for Eq. (13) about (P_1/P_2) and $(P_1/P_3) = 1$.

There are only very small uncertainties in reading the difference in the two columns on the manometer, perhaps ± 2 mm for each. The uncertainty in reading the barometer is even less, perhaps ± 0.2 mm. Using standard equations for propagation of error from other references (Harris, *Quantitative Chemical Analysis*, another book that contains statistical equations, or CHEM 446 Home page), calculate the resultant uncertainty (both absolute and relative) in γ using Eq. (13) and Eq. (17). Compare this uncertainty with the standard deviation and relative standard deviation of your measurements.

References

1. S. Glasstone, *Textbook of Physical Chemistry*, 2nd Ed., van Nostrand, New York, 1946 and references therein.
1. G. L. Bertrand and H. O. McDonald, *J. Chem. Ed.* 63, 252 (1986).
2. D. P. Shoemaker, C. W. Garland, J. I. Steinfeld, and J. W. Nibler, *Experiments in Physical Chemistry*, 4th Ed., McGraw-Hill, New York, 1981.